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EXTENDED APPEARANCE POTENTIAL FINE STRUCTURE ANALYSIS:

OXYGEN ON ALUMINUM (100)*,+

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ABSTRACT

To measure oxygen-aluminum separation at Al (100) surfaces disordered (LEED beams extinguished) by reaction with oxygen, we analyzed the extended appearance potential fine structure above the threshold for electron-bombardment excitation of the O 1s core. Explicit calculation shows the outgoing electron has angular momentum $\ell = 0$, allowing simple Fourier inversion of the fine structure. The separation, 1.98 ± 0.05 Å, indicates oxygen lies under the top layer, a result undetectable in EXAFS measurements on thicker films.

The reaction of a (100) single crystal aluminum surface with oxygen is observed to completely suppress the low-energy electron diffraction (LEED) pattern, once oxygen coverages exceed roughly a monolayer (1). This loss of long-range order renders techniques such as LEED and ion backscattering incapable, even in principle, of determining the oxygen-metal distance. In a recent paper, however, Stöhr et al. (2) have demonstrated that surface extended X-ray adsorption fine structure (EXAFS) analysis, using monochromatized synchrotron radiation, can provide information on the oxygen-metal distance in aluminum oxide layers approximately 30 Å thick. The present paper demonstrates that extended appearance potential fine structure (EAPFS) analysis can be used to obtain interatomic distances for much thinner layers. It is therefore well-suited to studies of overlayers and is capable of extracting information inaccessible to probes requiring greater thickness. Moreover, EAPFS requires only an inexpensive electron source for excitation.

Fine structure in the excitation probability of core states by electron bombardment is observed to extend for hundreds of volts above the excitation thresholds or "appearance potentials" (3). This fine structure results from the interference of an outgoing spherical wave of a scattered electron with backscattered components from neighboring atoms. It is therefore analogous to EXAFS (4), and interatomic distances can accordingly be extracted by essentially the same Fourier inversion techniques. EAPFS has been used previously to determine nearest-neighbor spacings in the surface region of polycrystalline vanadium (5) and other transition metals (6), but this experiment is the first to illustrate clearly its sensitivity to thin overlayers and to demonstrate fully the existence of fine structure oscillations analogous to EXAFS.

The surface sensitivity is a consequence of the short mean free path for inelastic scattering of the incident electrons. Similar sensitivity to the surface region has been achieved in EXAFS by using the Auger yield to signal the creation of core holes in iodine adsorbed on silver (7). The same technique cannot be applied to oxygen adsorbates, however, since the apparent Auger yield is strongly modulated by core electrons photoemitted from the substrate (2). The core-state photoelectron peaks are swept through the window of the electron analyzer as the incident wavelength is varied. To avoid this difficulty, Stöhr et al. (2) employed the partial yield technique (8), in which the analyzer window is set in the inelastic tail of the spectrum. Thus, in order for an adsorption event to be monitored, it must occur sufficiently far inside the solid for the excited electron to scatter inelastically: events occurring within one inelastic scattering mean free path of the surface are unlikely to be measured. Hence, this approach samples significantly more deeply than the appearance potential technique.

The excitation of a core state by electron bombardment in metals is contrasted to X-ray absorption schematically in Fig. 1. In the X-ray case a single electron is ejected; its energy is the difference between the incident photon energy and the core binding energy. In the appearance potential experiment, the final state energy is divided between two electrons. However, differentiation of the yield with respect to energy produces a signal which strongly emphasizes the situation in which one of the final-state electrons lies at the Fermi energy or, more generally, the lowest unoccupied state (3, 9, 10). Thus, it is the first derivative of the yield which is analogous to the undifferentiated absorption spectrum in EXAFS.

The measurements reported here were obtained with conventional hemispherical-grid LEED optics. The experiment consisted of measuring the second derivative of the elastic yield as a function of the energy of the incident electrons. The elastic yield is obtained by biasing the retarding grids a few volts positive with respect to the emitter of the electron gun. Electrons that have lost more than a few electron volts in their interaction with the crystal are thus repelled, and the current to the LEED screen measures the elastic scattering yield. At the thresholds for inelastic scattering from core states, the elastic yield decreases (11). Extended appearance potential fine structure in elastic yield measurements has been reported previously by Jach and DiStefano (12), whose measurements extended to only about 150 eV above the edges they examined. Substantial multiple scattering near the excitation threshold seriously complicates analysis in the lower half of this region, and may explain their failure to obtain spacings that appear reasonable. In the measurements reported here, the derivative was obtained by superimposing a small sinusoidal oscillation on the sample potential and detecting those features in the collected current that exhibited the same variation or, in the case of the second derivative, its second harmonic.

By operating the LEED optics as a retarding-potential analyzer, we obtained the Auger electron spectrum of the surface and thus could monitor surface coverage. A clean aluminum surface was obtained by argon ion bombardment and annealing. After exposure to 120 Langmuirs of oxygen, the LEED beams were completely extinguished;

according to Gartland (13) this exposure corresponds to about 1.5 equivalent monolayers of oxygen. An appearance potential spectrum, consisting of the second derivative of the elastic yield, was obtained over an incident electron energy range of 500 to 1000 eV. This range includes the oxygen 1s edge at 533 eV and its associated fine structure (Fig. 2). There are no other edges in this range. The aluminum 1s is at 1540 eV and the Al 2p occurs at 73 eV. Some fine structure from the Al 2p presumably extends beyond the O 1s, but is too weak to interfere with measurements of the oxygen spectrum.

Variations in the elastic yield resulting from diffraction of the incident electron beam often obscure appearance potential features in the energy range up to perhaps 600 eV. In the case of the Al (100) surface, however, the loss of long range order resulting from the interaction with oxygen was sufficient to almost completely suppress these diffraction variations. The remaining slowly-varying [compared with the fine structure] background variations were removed from the data by first subtracting a least-squares-fit cubic polynomial from the data to remove very coarse variations[5] and subsequently applying a high-pass digital filter[6] (Fig. 3). Taking a third derivative would serve the same function, but enhances noise and has less physical basis.

A serious question remains. The phase shift appropriate to the central (absorbing) atom and the surrounding backscattering atoms differs for the various angular momentum components of the outgoing electron. Given a core electron with angular momentum $\ell = 0$, the dipole selection rule indicates that X-ray excitation must place it in an $\ell = 1$ state. In the case of electron excitation, an explicit calculation is required to find the relative

coupling to each partial wave of the higher-energy final-state electron. To make this determination, we obtained the core state to be excited from a Hartree-Fock-Slater calculation (14). For the other three wave functions, we used orthogonalized plane waves decomposed by angular momentum about the central atom. We then calculated Coulomb potential matrix elements (10). The results (15) show: 1) orthogonalization to the core state is indeed crucial; 2) matrix elements are smooth, slowly-varying functions of energy; and most importantly, 3) the matrix element coupling to the $\ell = 0$ higher-energy outgoing final state is overwhelmingly dominant, so that the oscillatory part of the transition rate contains a single term (16) of the form

$$F(k) \sum_j \frac{\sin[2kR_j + \phi_j(k)]}{k\,R_j^2}$$

where k is the momentum of the outgoing state, F(k) is a slowly varying envelope function with k-dependence dominated by Debye-Waller effects, R_j is the distance to the jth shell of surrounding atoms, and ϕ_j is the k-dependent phase shift.

One of us (G.E.L.) has calculated the $\ell = 0$ combined phase shift for the central (oxygen) and backscattering (aluminum) atoms using self-consistent non-relativistic Hartree-Fock-Slater ($\alpha = 2/3$) atomic potentials overlapped in the appropriate configuration. These results agree with calculations by Teo and Lee (17). Using the threshold for the oxygen 1s excitation as the momentum zero (18), we took an optical Fourier transform of the data from 70 to 450 eV above the edge, weighted by the cube of momentum in standard EXAFS fashion (19).

The magnitude of the transform is plotted as a function of interatomic spacing in Fig. 4. A single dominant peak, presumably corresponding to the nearest-neighbor oxygen-aluminum distance, is located at $1.98^{\pm}0.05$ Å. This value corresponds to the longer of the two Al-O spacings in bulk Al_2O_3, viz. 1.97Å; [the shorter is 1.86Å] (20). Our value is consistent with the number 2.02Å proposed in SW-CSF-$\chi\alpha$ calculations of low-coverage O on Al(100) (21). Since the longer Al-O spacing in Al_2O_3 corresponds to the oxygens lying between two Al atoms (rather than between Al and a vacancy), (22) our result supports the idea that the adatoms go under rather than on top of the first Al layer. This picture had been advanced earlier based on the decrease in work function with oxidation (23) and on SIMS results (24). The EXAFS result for the thick oxide layer was 1.91Å (2), the average of the two bulk spacings, and thus was insensitive to this surface-related feature.

The indicated error bars are a conservative estimate. The peak is shifted by less than 0.03Å over a wide range of filter parameters (22). The principal error may lie in our use of calculated (rather than experimentally derived) phase shifts.

Our measurements relied heavily on the disordering of the surface by oxygen to suppress diffraction variations in the elastic yield. Such variations are absent in appearance potential spectra obtained using the soft X-ray yield. EAPFS studies of low energy edges will therefore have to rely on the soft X-ray method in most cases. The present results, however, demonstrate the feasibility of the EAPFS technique for the study of overlayers. The use of electron-bombardment excitation makes the technique available to essentially any surface physics laboratory.

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FIGURE CAPTIONS

Fig. 1

Energy level diagram comparing the excitation of a core
level by a photon (left side) to excitation of the level
by a high energy electron (right side). In the latter case,
because both the incident electron and the ejected core
electron must be accommodated in states above the Fermi level,
the final state is a two-electron state. Differentiation
with respect to incident electron energy selects the situa-
tion in which one electron is near E_F and the other carries
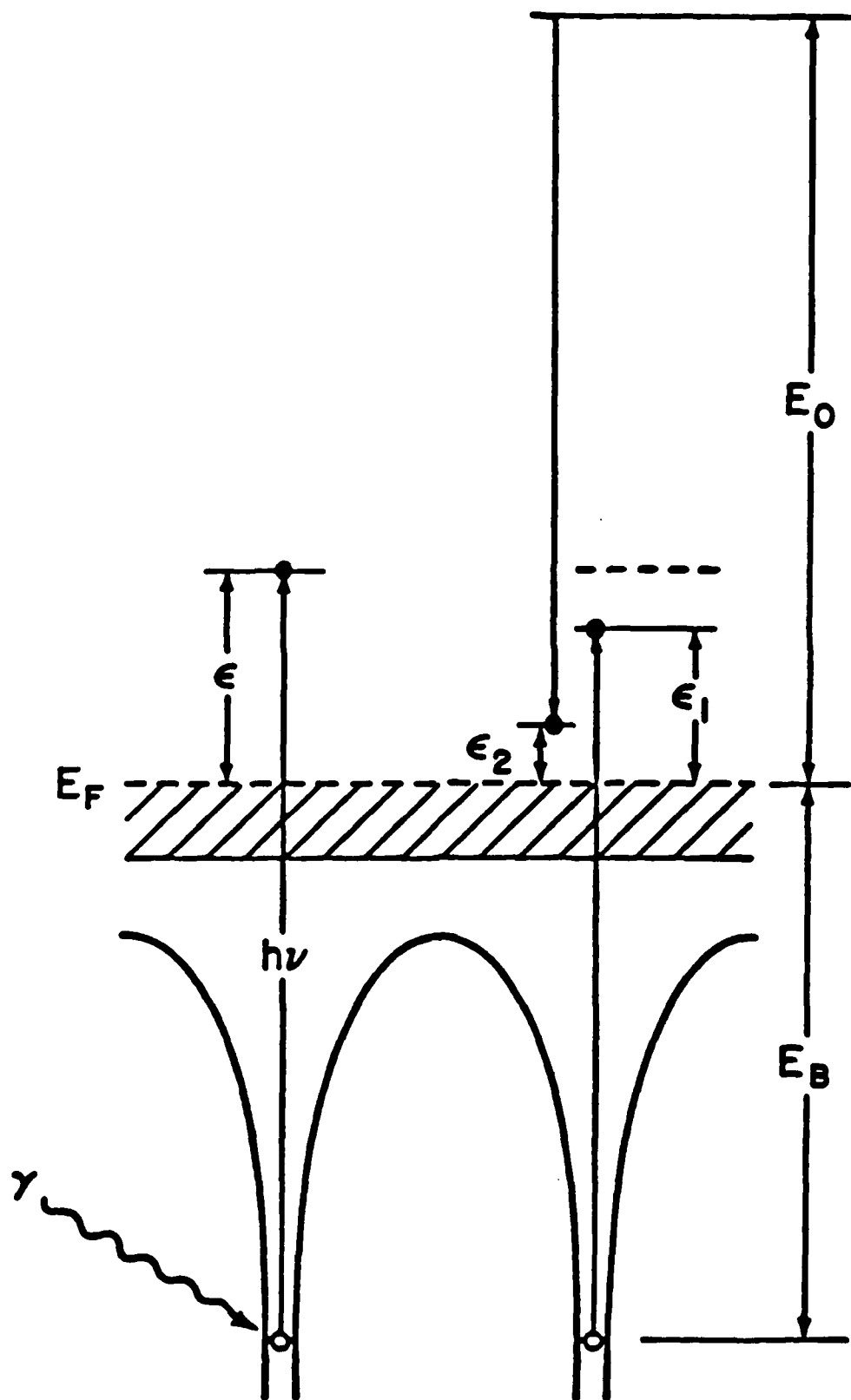the remaining energy (as in the case of X-ray excitation).

Fig. 2

Second derivative of the elastic yield of the oxidated Al(100)
surface, plotted as a function of incident electron energy.
The O 1s appearance potential edge is at 533 eV (correct-
ing for the emitter work function). Fine structure extends
several hundred volts above the edge, but the periodic vari-
ations are masked considerably by the slowly-varying back-
ground.

Fig. 3

Extended fine structure associated with the O-1s edge plotted in Fig. 2. The first 70 eV of data above the edge has been excluded to avoid complications related to multiple scattering. A polynomial subtraction and digital filtering technique have been applied to further suppress slowly-varying background variations.

Fig. 4

Optical Fourier transform of the data in Fig. 3, including calculated phase shifts for an O 1s core and Al backscatterers. The single peak at R=1.98$^{+}_{-}$0.05 Å, is taken as the O-Al spacing in this thin aluminum oxide layer, indicating that the O lies under rather than over the top layer of Al. See text for details.
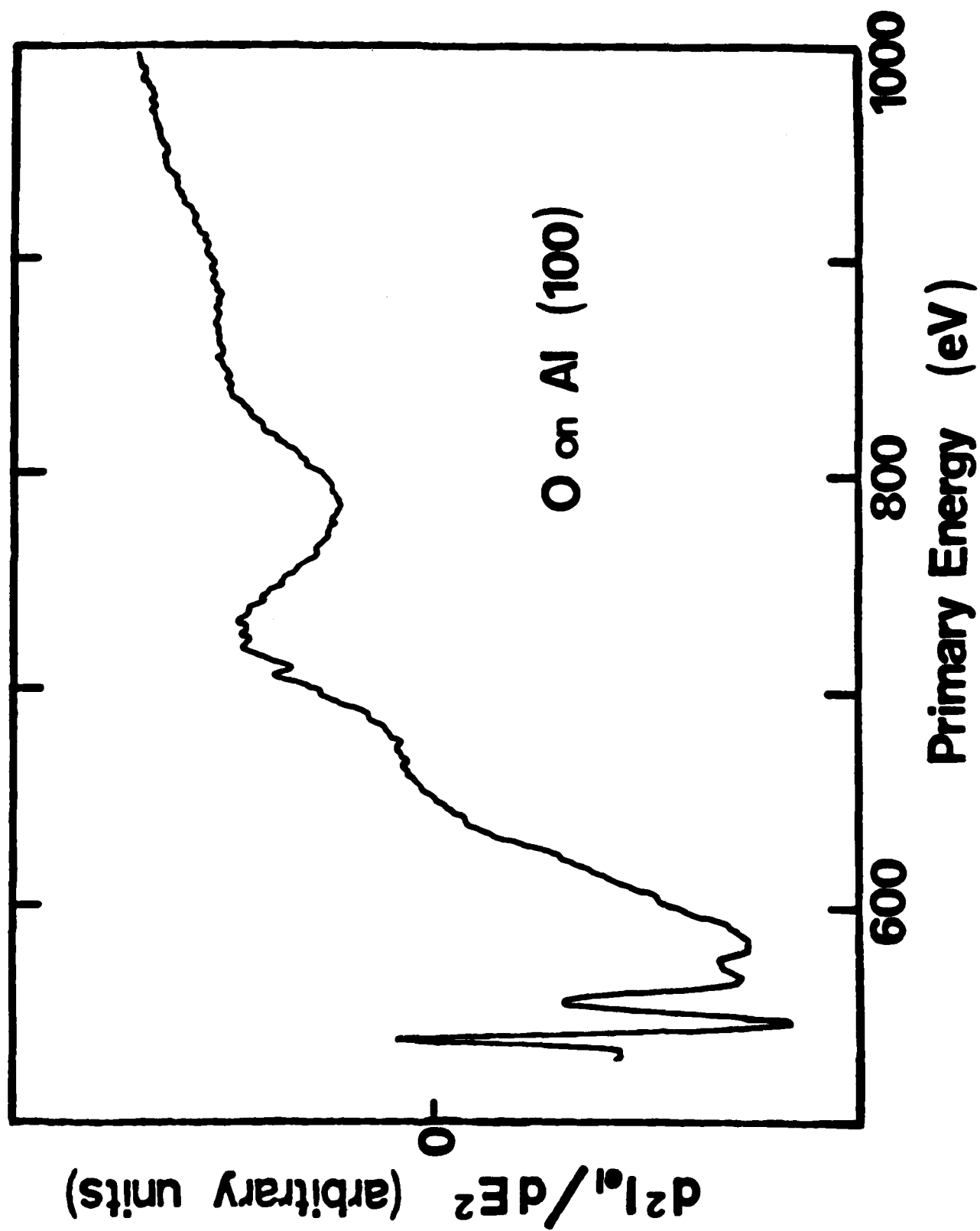
Figure 2   den Boer et al.   PRL

O on Al (100)

Primary Energy (eV)

$d^2 I_{el}/dE^2$ (arbitrary units)

0

O on Al (100)

Primary Energy (eV)

d^2I_{el}/dE^2 (arbitrary units)

0

600

800

1000